6-1990

Analysis of dolemitic limestone ore using direct current plasma spectroscopy

Edward M. Kulback
Union College - Schenectady, NY

ANALYSIS OF DOLEMITIC LIMESTONE ORE USING DIRECT CURRENT PLASMA SPECTROSCOPY

by

Edward M. Kulback

* * * * * * * * *

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

Union College

June 1, 1990

Abstract

KULBACK, EDWARD M. Analysis of Dolemitic Limestone Ore Using Direct Current Plasma Spectroscopy June 1990.

Four samples of dolemitic limestone ore, provided by the Thorne-Smith Company were analyzed for trace elements. Composition of limestone is important because this ore is often found with ground water (a primary source of drinking water); and in acidic conditions, certain elements can leach out of the ore and into the water supply, possibly in toxic levels, depending on the element. The elements that were found are: aluminum, iron, manganese, tin, and chromium. This last element is of particular concern because it appears in the ore in relatively high concentrations, and chromium can be a very toxic substance if its concentration is above 0.5 micrograms per liter of water.

The Thorne-Smith Company provided the compositions of their ores as weight percents of silica, MgO, CaO, and R_2O_3. The R_2O_3 term takes into account all the trace elements. The goal of this project was to assign actual oxides to this term. The elements listed above comprised 60-90% (depending on the sample) of the trace element group.

Using this data, a local (upstate New York) sample of limestone ore was analyzed for some of the elements listed above. The elements were found in the same approximate concentrations as they were in the prepared samples. This means that a model of limestone can be

made up, that indicates probable levels of trace elements in dolemitic limestone ore.

All samples were analysed on the SpectraSpan IV, a direct current argon plasma spectrometer. The SpectraSpan was chosen because it provided excellent detection limits, and gave superior resolution and dispersion. These qualities of the instrumentation allowed for a good quantitative analysis of the ores. This project was as much a learning experience in operating the instrument, as it was in analyzing the ores.

Acknowledgements:

At this point I would like to thank the following people for their assistance that they've given me over the past year:

Professor R. W. Schaffaer for giving me the opportunity to do research with him. I would also like to thank Prof. Schaffaer for bestowing upon me his trust and allowing me to conduct this project in a manor that I saw fit.

S. Sweeney, G. Gailliard, J. Hurd, and the rest of the Chemistry Department at the Schenectady Materials and Processes Laboratory for providing me with standards, literature, and their knowledge of the DCP.

The entire Chemistry Department for doing their job and doing it well. Believe it or not, I did learn a thing or two.

I would also like to thank my parents for their generous monetary contributions.

This paper is dedicted to my aunt, Audrey Heyer.

Table of Contents:

Introduction:

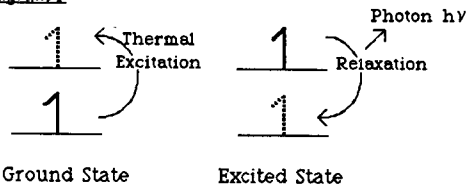
The main goal of this research project is to determine quantities of trace elements in dolemitic limestone ores. Limestone ore is comprised of mostly calcium carbonate; dolemitic limestone contains large amounts of magnesium carbonate in addition to the calcium carbonate. The reason for wanting to know what else is in the ores is two-fold. First, and most important, is that dolemitic rock is often found with natural groundwater, which is the primary source of drinking water[1]. Groundwater usually contains larger amounts of trace metals due to its prolonged contact with rocks and minerals, which may house these metals.[2] Therefore, the importance of knowing the composition of the limestone is obvious. Limestone is comprised of mostly calcium carbonate, some magnesium carbonate, and silica. But, there is more to the limestone; certain oxides will bind themselves to the silica. This leads to the second reason of analyzing the ores, scientific curiosity. How can the silica be best stripped of the metallic oxides and what are these compounds?

As stated above, the driving force behind this project was to see if there are any toxic compounds in the limestone and in what quantities. The presence of these impurities in the water can be attributed to the leaching of salts from the the limestone[3]. And in today's society, with the air pollution, and acid rain problem, this leaching factor can be quite large; and this means that even elements that are beneficial in small quantities, can become toxic in large amounts.[4]

Of particular concern, is the concentration of chromic oxide in the limestone. The maximum limit of chromium in drinking water is 50 parts per trillion, extremely low.[5] If there is chromic oxide present in the limestone in any kind of considerable amounts, it may leach out into the water in higher concentrations than allowable. Even if this happens though, there is no need for major health concern, this limit is only one-hundredth of the maximum no-observed-adverse-health effect concentration.[6]

To analyze these ores, a very sensitive, quantitative, method is needed, since small amounts (possibly as low as 10 parts per billion, ppb) need to be detected. The instrumentation to be used is a direct current argon plasma spectrometer (DCP). DCP is an emission spectrometer that thermally excites the sample through use of a plasma. When a sample is excited, a large population of electrons will be thrown into higher energy orbitals. When an electron relaxes back to its ground state configuration, it emits a photon of light with a specific, characteristic wavelength. One can count how many photons are released at this wavelength, and this will be directly proportional to the concentration of the element in question in the sample. Diagram 1 shows a simplification of the whole process.

Diagram 1



In reality, there are many transitions that the electron can go through, each one requiring a different mount of energy, and each emitting a characterisitc photon on relaxation. What this means is that each element can emit at several different wavelengths. By setting the instrument to 'look' for a particular wavelength, it will count the photons emitted, and transform this number into a concentration.

The benefit of using DCP over other types of spectrometers is that DCP can achieve very high temperatures in the plasma. A conventional gas/air flame can achieve temperatures of 2000 K, advanced flames can reach 3000 K, the plasma reches temperatures of 6000 K in the excitation region. These higher temperatures allow more sensitive detection because at higher temperatures there are more electrons in the excited state. The Boltzman equation provides proof of this: $N_e/N_g = e^{-(E_e-E_g)/kT}$, where N_e is the population of the excited state, N_g is the population of the ground state, E_e and E_g are the respective energies of these states, k is the Boltzman constant and T is the temperature. As can be seen, an increase in the temperature will increas the ratio, causing the excited state to become more populated.[7]

A relative of the DCP is the ICP, or inductively coupled plasma spectrometer. The ICP uses radio frequencies to ionize the argon gas and create the plasma. ICP reaches temperatures of up to 8000 K in the excitation region.[8] This high temperature provides a higher concentration of electrons in the excited state, which is beneficial. But, these high temperatures can also overpopulate the excited state and the excited electrons may interact with each other and give unexpected results. ICP is also a more expensive instrument and more coslty to operate than the DCP.

As stated before, the sample is excited via thermal means, the plasma. The argon plasma is formed by sending a direct current through an argon gas stream. The current will ionize the argon forming a plasma.[9] Later sections will provide more detail of how the whole instrument works.

Another reason for choosing the DCP as the testing instrument is because it has an excellent optics section consisting of a Czerny-Turner type of spectrometer with an echelle grating. This set-up gives excellent resolution and dispersion. This, too, will be discussed later.

Now that a basic overview of what this project is intended to do, why it's being done, and by what means it's to be carried out have been stated, a more detailed explaination can follow.

Theory of the DCP Spectrometer:

The plasma:

The plasma is ignited by separating three electrodes in an argon atmosphere while conducting a current of approximately 15 amperes. Since the power supply is a constant current supply, the voltage output must increase quickly as the elctrodes separate so as to ionize the gap and keep the current constant at 15 amps.[10] There are two graphite anodes, and one tungsten cathode. When the instrument is in the READY position, the back anode is in contact with the cathode. Upon switching to the RUN position the electrodes are retracted and the cathode is raised. See Diagram 2 in Appendix A (reproduced from SpectraSpan..Operating Manual).

The current passing through the argon heats the gas and sustains the plasma. The temperature in the plasma can reach 10,000 K and 6000-7000 K in the excitation region. As stated in the Introduction, this high temperature accounts for the instruments above average sensitivity.

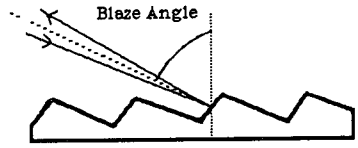
The samples, which must be liquid, are converted to an aerosol by a ceramic nebulizer. The nebulizer works at approximately 20% efficiency. The sample spray is carried up to the plasma by a stream of argon gas. This process results in a phenomenon called a thermal pinch. The pinch arises because the gas carrying the sample is cooler and has a lower conductivity than the hot plasma. Therefore, the current is contained to as close as possible to the center of the plasma. The pinch constrains the plasma, holding it to a narrow volume. The

result of this is a higher temperature, more stable, plasma, than if there was no thermal pinch.[11] The excitation region is just below the plasma because this is where the sample concentration is greatest and the background is minimized.

The optics:

The instrument employs a Czerny-Turner type of spectrometer with an echelle grating, and a photomultiplier tube as the detctor. Refering to Diagram 3 (in Appendix A), the emitted light enters the optics section throught the input slit and is refracted by the prism located in front of the echelle grating. The prism serves to separate orders of light while the echelle grating does the finer wavelength separation. The echelle grating is excellent for the finer separations because it provides high resolution and high dispersion (or low reciprocal dispersion). Resolution is the ability of the monochrometer to separate adjacent images having slightly different wavelengths. Dispersion is the ability of a monochrometer to separate different wavelengths.[12] The echelle grating differs from normal gratings in several areas. First, the blaze angle is greater; and the short side, not the long side, of the blaze is used (see Diagram 4 on the next page, reproduced from Instrumental Analysis, p 300).

Diagram 4



Echelle Grating

Also, the groove density is a lot lower for the echelle grating, allowing for better separation of UV/visible signals.[13] On reflection off the grating, the light once again passes through the prism which arranges the orders into a raster configuration. Whereas conventional spectrums are dispersed into a line and occupy considerable length, the echelle grating with prism compacts this into a two dimensional (4" x 5") raster configuration (see picture on next page). The shortest wavelenghts appear at the top, and the longest at the bottom. This set-up gives resolution ranging from 0.001 nm to 0.003 nm. The reciprocal linear dispersion ranges from 0.062 nm/mm to 0.25 nm/mm. [14]

The light then passes through the exit slit and to the detector, which has been pre-set on a certain wavelength. The detector here is a photomultiplier tube, PMT. The PMT has certain advantages over other types of detectors because it can take a very weak input and transform it into a powerful electrical signal. The photon emitted from the sample strikes a photoemission cathode. This will release an electron, which is accelerated toward a dynode by a potential gradient. When this electron strikes the dynode it will release several more

electrons. These electrons are then accelerated toward a second dynode due to a potential gradient. Each of these electrons will in turn release several more electrons. This process goes on through a total of nine dynodes, each with a potential of 90 volts greater than the previous dynode. The build up of electrons, due to one photon, can be as high as 10^6. This wave of electrons is finally picked up by an anode and the current produced is measured.[15] This signal is then electrically enhanced and sent toward the instrument's computer. The internal computer will compare this signal to a calibration line that it has set up with information from the standards and display the concentration. The instrument can do this since the current is directly proportional to the number of electrons released, which is directly proportional to the number of photons emitted, which is directly proportional to the concentration of the sample.

Procedure:

This section will be divided into the following sub-sections: preparation of glassware, preparation of the samples, preparation of standards , and running of samples.

Preparation of glassware:

In this experiment, trace amounts of elements are being analyzed, therefore, the glassware used must be as clean as possible. The volumetric flasks and beakers to be used are rinsed with concentrated nitric acid. This washing involves adding around 10 mL of acid to the glassware and swirling it around so as the acid makes contact with the entire container. Then the acid is dumped and the glassware is rinsed with tap water five times (to expel the acid) and with deionized water at least ten times to ensure that all the tap water has been expelled. The glassware is now considered clean and ready for use. This procedure is done anytime glassware is used.

In the preparation of the samples, glassfilters are used. These are cleaned by drawing concentraed nitric acid through the filter via a suction. Then tap water and DI water are pulled through the filter in the same proportions as used above. The Erlynmeyer flask used in the filtration is cleaned the same way as the other flasks are cleaned.

Preparation of samples:

The preparation of the samples is perhaps the most important step of this research project. Since the samples are of dolemitic limestone ores, there will be high amounts of silica present. The

elements being tested for will tend to bind to the silica. So the problem here is to find a way to strip the metallic elements to be analyzed away from the silica. Hydroflouric acid will dissolve the entire ore, including the silica; but, HF is very reactive and difficult to use. This acid will react with glass, so all solutions would have to either be prepared in special types of plastic or platinum, which is very expensive. Also HF, when used to dissolve the silica, would release silicon tetraflouride fumes which are dangerous. Used instead, is boiling concentrated nitric acid. Nitric acid will strip the silica with various degrees of success. S. Lipsky found that multiple boiling concentrated nitric acid washings proved to be the best way to prepare the samples.[16] Since this process was fairly long and involved many steps, where error can occur, and since Lipsky was preparing larger amounts of sample, an easier method was the goal. Three methods are tested.

Method 1 resembles the Lipsky method. A 0.20g sample is placed in a clean 100 mL beaker. Add 20 mL of concentrated nitric acid and boil this solution to half-volume (10 mL). After boiling, let the beaker sit, unagitated for 15 minutes, so the silica residue can settle. Decant the supernatant liquid though a fine fritted glass filter hooked up to a vacuum source. Make sure no solid particles are accidently spilled out. Upon final filtration, wash the beaker and solid residue three times with 1M nitric acid and once with DI water. Pour the solution collected after filtration into a 100 mL volumetric. Wash the Erlynmeyer flask used in the filtration step three times

with DI water.

Method 2 is a modification of Method 1. Here instead of using three 20 mL acid washings, two 30 mL acid washings are used. The rest of the procedure stays the same.

Method 3 consists of one washing of 60 mL of nitric acid, with the filtration and washing steps the same as reported above.

The three solutions produced by the above method are then quantitatively transferred to clean 100 mL volumetrics and diluted with DI water to the mark. The solutions are run twice through the DCP and analyzed for chromium as a test to see which method best stripped the silica. The average results follow:

Method 1	0.00691 % Cr
Method 2	0.00682 % Cr
Method 3	0.00670 % Cr

The data shows that Method 1 is the most effective means of stripping the silica. From now on all samples will be prepared using Method I.

Preperation of standards:

All stock standard solutions are prepared in clean 100 ml volumetric flasks. Only high purity samples are used to make the standards. These samples are dissolved in concentrated nitric acid. Nitric acid is used so both the standards and the limestone samples are in the same matrix. To prepare some of the samples, a combination of concentrated hydrochloric and concentrated nitric acid needed to be used. The concentration of each stock solution is 1 part per thousand (except aluminum and iron). This high

concentration was used to prevent substantial lose of the standard due to absorbtion through the glassware. The stock solution is then used to prepare dilute standards. These dilute standards have to be made up daily since their concentrations (down as low as 100 ppb) can be drastically affected due to absorption through the glassware.

Running samples:

Once the DCP has been stabilized and electronically peaked on a certain wavelength, the testing of the samples can be done. The first step involved is to set up an internal calibration line. This is initially done in a semi-quantitaive way. A standard of reasonably high concentration, 500 - 1000 ppm is used as the high standard and DI water is used as the low standard, 0 ppm. The samples are then run, and the results recorded. New standards are now made to 'straddle' the reported value. For example, if on the first pass the standards were 0 ppm and 500 ppm and the sample came to be 243 ppm, the new standards would be 200 ppm and 300 ppm. This procedure gives more precise readings of the actual sample concentration. The reason for this is that any flucuations in the concentrations of the standards will be less pronounced in the straddle method.

Operation of the DCP Spectrometer:

Operation of the DCP is not complicated, but strict adherence to certain procedures is necessary for successful use of the instrument. The following are step by step instructions on how to use the DCP.

Before startup:

There are certain items that must be checked before igniting the plasma. There must be a source of pure argon with a regulator attached. Cooling water must be flowing through the instrument. All tubing should be clean and operational. The three electrodes should be clean and usable and housed in clean ceramic sleeves. Also a vent should be present to take up the exhaust.

Start up:

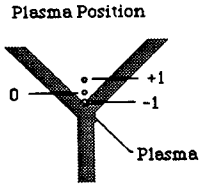
Turn on the peristalic pump and shut the safety cover. Make sure the ON/OFF switch is OFF, and the RUN/READY switch is READY. Turn the argon source up to 60 p.s.i.. Now, turn the instrument ON and press the PWR and PLS buttons. The sound of flowing argon gas and electricity should be heard. Check the pressure of the nebulizer and sleeves on the side of the instrument. They should be around 40 and 45, respectively. Place the sample intake tubing into a beaker of DI water. Next, SLOWLY lift the RUN/READY switch to RUN. The plasma should now be formed, indicated by a flame in the formation of an inverted 'Y'. If not, switch back to READY and try again. An inverted image of the plasma can be viewed ; it should be stable. If the plasma is jumping around or if a high-pitched whistling noise is heard, adjust the pressures on the side. If the pressures are too high

they will 'blow out' the arc; if the pressures are too low, the plasma will not form. Once the plasma is ignited, let it stabilize for about 20 minutes.

Choosing a wavelength:

In choosing a suitable wavelength for analysis, it's recommendable to use The Handbook of Spectral Line Characteristics for the DC Plasma / Echelle System, published by Spectrametrics, Inc., Andover Massachusetts. Here, they list all major emission lines for the elements and information about that line, including: the detection limit, the linear dynamic range, plasma position, and any interferences (See example in Appendix A). The detection limit conveys the lowest possible concentration that the detector can detect at that wavelength. The linear dynamic range is perhaps the most useful piece of information provided. The range states that a plot of the concentration versus photons counted will be linear between the concentrations listed (there is an example of the linear dynamic range in Appendix B). This is crucial since the instrument will always assume that this is a linear plot, and if in reality it is not, the results will be inaccurate. The next piece of information provided is the plasma position. In most cases this value is zero, meaning that the entrance slit should be placed just below the crux of the inverted Y. Values of -1 or +1 indicate that the slit should be either closer to or further away from the plasma. See Diagram 5 on the next page (reproduced from The Handbook of Spectral Lines...).

Diagram 5



Finally, the last piece of information to be used is that of possible interferences. This list any compounds that also emit at the wavelength in question. If this book is not available, a list of elements and their wavelengths will be. If this is the only means of information, the highest energy (UV) wavelength should be chosen to eliminate as much interference from the matrix as possible.

Peaking the instrument (assuming the instrument has been stabilized):

Once a suitable wavelength has been chosen, set this value on the scroll in the front of the instrument by using the two thumbwheels. Set the following switches as stated: (auxiliary control panel) STD. DEV., up; DIAG., up; AVG. ONLY, down; LED, down; XMIT, down; PRINT, down; VOLTAGE X 100 at 8; TEST CURRENT at PMT; (main control panel) MODE at 1, TIME and REPEAT anything except zero. Now, intoduce a peaking solution into the sample intake tubing. The peaking solution should be a solution of the element in queston, made from a pure standard, and of moderately high concentration.

Let the plasma stabilize with the new solution for about 2 minutes. Then, press the A/R, auto-range, button. The instrument is

now assigning this concentration a value of 0.45 milliamps. Once it has done this, press the SMP, sample, button. The analog output should show about 0.45 as also should the digital output. It is fine if the outputs are slightly flucuating. Fine-tuning of the instrument now must take place. Move the fine-adjusting thumbwheels so the output readings increase. If it goes off scale, lower the VOLTAGE X 100. Adjust until any slight change of wavelength will lower the output. The instrument is now peaked. Press RST, reset, to stop this process. Remove the peaking solution, clean the tubing with a tissue, and put DI water back on line. As a test, press the SMP button with the DI water as the sample, the output should read zero (or close to it), if not there will be considerable background interference.

Setting up the standard calibration line:

Make the following changes to the controls: VOLTAGE x 100 back to 8, MODE to integrate, TIME to 10, and REPEAT to 5, also press the CLR. MEM button to clear the instrument's memory. On the keypad enter the concentration of the high standard (any units), and press the ENT HI button, enter the value of the low standard and press the ENT LO button. Introduce the high standard, and allow the system to equilibrate. Press the A/R button and wait until the the digital readout returns the value of the high concentration. Clean off the tubing and input the low standard. Press the LO STD button, and wait until the value of the low standard is printed on the digital readout. What the instrument has done is assigned a certain electrical signal, from the detector, to the specified concentrations.

So now, when a sample is introduced, it will give an electrical signal which the instrument will place on this calibration line and calculate its concentration.

Running a sample:

Allow the instrument to intake the sample and equilibrate itself for a few minutes. Then press the SMP button, and wait until the digital readout presents the desired information. If the value of the concentration is outside the range of the high and low standards, remake the standards and re-calibrate the instrument. Then run the sample again. This is to get a more accurate result.

Shutdown:

Press the PWR and PLS buttons to turn off the computer and plasma. Then remove the DI water from the sample intake tubing, but do not turn off the pump. Turn off the main argon valve and let the lines bleed. Now switch the RUN/READY switch back to READY, and the ON/OFF switch to OFF. At this point, the pump may be turned off and release the clamp on the pump. Turn off the cooling water and exhaust fan. Everything should now be off.

Miscellaneous:

At all times, a liquid sample must be taken in by the instrument. If no sample is running, then DI water should be used.

If the STAT, status, button lights up during operation, the instrument is indicating that there is a problem with the current set-up. For example, if the operator accidently inserts the high standard when the low standard should have been inserted, the

instrument will recognize this, and warn the operator. To find out what the error is, press the STAT button and a number between one and eight will appear on the digital display. This number corresponds to a certain problem. A list of possible status problems appears in the manual and on the instrument itself, inside the auxiliary control panel. Make the appropriate corrections and continue.

In this project, there was no printer to make hard copies. If a printer is available, and a hard copy is desired, set the PRINT switch, up.

Also availible to the operator is a photographic attachment. This will take Polaroid pictures of the spectrum and is useful in qualitative work. It was not used in this project.

If there are any other problems, consult the instruction manual.

Results and Discussion:

To accomplish the goal of this research project, which was to analyze dolemitic limestone ores for trace elements, samples of clean ore are needed. Clean in the sense that there are no major impurities in the sample. For example, gypsum ($CaSO_4$) is often found with the ore of interest. The Thorne-Smith Company supplied the limestone rock needed. The samples, which have the texture of sand, are simply labelled Limestone #24, #25, #26, #28. Along with the sample is a list of major components of the rock, see Table I.

Table I

Sample	%CaO	%MgO	%silica	$\%R_2O_3$	%L.o.I.	Total
24	43.38	5.36	7.58	3.47	40.07	99.86
25	41.71	4.77	9.63	1.63	40.10	97.84
26	40.58	7.23	10.78	1.14	40.27	100.0
28	40.61	8.33	7.83	2.05	41.14	99.96

As can be seen, the major elements, calcium and magnesium, are listed in the oxides. R_2O_3 is the number that is of interest to this project. This percentage takes into account all trace elements that appear in the ore. These elements, too, are reported as their oxides. L.o.I. is loss on ignition, this percentage takes into account the fact that when the sample is heated to very high temperatures (such as in the plasma) carbon dioxide will be released from the original $CaCO_3$ and $MgCO_3$. Due to statistical error, not all totals add up to 100%.

My predecessor, S. Lipsky, found that a bulk of the unknown R_2O_3 is the oxides of iron and aluminum[17]. But there still is a

considerable amount of this R_2O_3 term that is unaccounted for. By naming these other oxides, a model can be created that will state possible ranges of these oxides in all limestone ore.

Before any actual analysis can be done, though, certain tests of prescision must be carried out by the operator. Analysis for calcium in tap water is an excellent test, since calcium lines are easy to find, and there is a considerable amount of calcium in tap water. Five tests were done on tap water, three at 445.4 nm, and two at 422.6 nm. Success of this analysis would state that the operator and instrument could produce repeatable data, even at different wavelengths. Table 2 has the results.

Table 2:

Line (nm)	ppm Ca
445.4	49.7
	48.9
	50.4
422.6	50.5
	49.4

Statistical analysis of this data shows that the instrument has a natural variability of about 4%. This error will be carried through all calculations.

The elements that are tested for in this experiment are: Fe, Al, Cr, Mn, Sn, and V. Even though iron and aluminum were already tested for by Lipsky, they were analyzed again for sake of completeness. All values agreed, except Sample 28. Since there were no errors or problems with the running of the test, the data

retrieved by this project will be taken as correct. On the next page is a list of the compounds used in preparing the standards. The list will be in the same fashion as seen below.

Source: from what compound was the standard made

MW: molecular weight of the compound in grams per mole.

grams: how much of the compound was used.

ppt R: the concentration of the element R in ppts.

Line: the wavelength, in nm, at which the element was analyzed

Analysis for chromium:

Source:	$K_2Cr_2O_7$ (dried)	Line: 425.4
MW:	294.19	
grams:	0.2831	
ppt Cr:	1.001	

Analysis for manganese:

Source:	$MnSO_4$ (dried)	Line: 403.0
MW:	150.99	
grams:	0.2752	
ppt Mn:	1.001	

Analysis for tin:

Source:	$SnCl_2 . 2H_2O$	Line: 286.3
MW:	225.64	
grams:	0.1901	
ppt Sn:	1.000	

Analysis for aluminum:

Source:	aluminum metal	Line: 396.2
MW:	26.982	
grams:	0.0103	
ppt Al:	0.103	

Analysis for iron:

Source:	iron metal	Line: 358.1
MW:	55.847	
grams:	0.0100	
ppt Fe:	0.100	

Analysis for vanadium:

Source:	Spex Standard	Line: 437.9 & 309.3
MW:	n/a	
grams:	n/a	
ppt V:	1.000	

The results from running the limestone samples, as stated in the earlier sections, yields concentrations in either ppm or ppb. These values must be converted to $\%R_2O_3$ (or $\%RO_2$ for Mn and Sn, because these metals form the IV oxidation state, not the III state). The results are in Table 3.

Table3:

Sample	$\%Fe_2O_3$	$\%Al_2O_3$	$\%Cr_2O_3$
24	2.70±.11	0.285±.011	0.0235±.0009
25	0.929±.037	0.251±.010	0.0094±.0004
26	0.411±.016	0.237±.009	0.0108±.0004
28	1.19±.04	0.213±.009	0.0081±.0003

Sample	$\%MnO_2$	$\%SnO_2$
24	0.0586±.0023	0.0484±.0019
25	0.0678±.0027	0.0478±.0019
26	0.0286±.0011	0.0428±.0017
28	0.0461±.0018	0.0434±.0017

Vanadium was run multiple times at different wavelengths and with different standards, but at all lines tested, there was considerable background and results could not be achieved. The reason for this is unknown. A possible source of this error was thought to be either dirty glassware or soiled instrument parts. New standards were made up in clean glassware; all replaceable parts of the instrument were replaced and all other parts were cleaned. Still,

the error persisted. The next possible source of error to be hypothesized was that the DI water was not pure. The ion exchange tanks were checked and the used ones were replaced. These tanks are the chief source of deionizing the water. This was to no avail, though, the problem was still present. The only reason that this error could remain is for it to be present somewhere with the instrument, either the computer or the optics section. My opinion is that a contaminant reached the optics section and is somehow creating a signal that is similar to the lines that vanadium would emit.

Table 4 shows a comparison of the reported $\%R_2O_3$ and the experimental range of $\%R_2O_3$ (from the data in Table 3), and the ratio of these numbers (%Exp / %Rep).

Table 4:

Sample	Reported %	Experimental %	Ratio
24	3.47	2.99 - 3.24	0.86 - 0.93
25	1.63	1.25 - 1.36	0.76 - 0.83
26	1.14	0.70 - 0.76	0.61 - 0.67
28	2.05	1.44 - 1.56	0.70 - 0.76

By using the information already obtained, the next goal is to see if the data in Table 3 can be used as a model for a limestone sample not from Thorne-Smith. A piece of local dolemitic limestone was obtained from the Geology Department at Union College. Several test were run on this ore, and the data is in Table 5.

Table 5:

Sample	$\%Fe_2O_3$	$\%Al_2O_3$	$\%Cr_2O_3$
Local	1.31	0.22	0.0059
25	0.93	0.25	0.0094

From Table 5, one can see that the oxides appear in this limestone ore in the same relative abundance as they appear in the Thorne-Smith samples (Thorne-Smith Sample #25 is listed as a comparison). This shows that chromic oxide (as well as iron oxide and aluminum oxide) does appear in naturally occuring limestone in relatively high concentrations.

Table 4 showed that the addition of all these trace elemental oxides does not add up to the full value of R_2O_3. Sample 24 comes the closest with 90% of the R_2O_3 term accounted for; while Sample 26 has only 64% of this term identified. This implies that there are still more elements in the ore that have so far gone undetected. Due to time constraints, further analyzation of the Thorne-Smith and local sample could not take place. Elements that would be of interest are arsenic and lead.

Conclusion:

This research project was intended to make quantitative statements about dolemitic limestone ores, while gaining experience on how to operate one of the most powerful analytical tools found in laboratories. Before the data is discussed, a brief overview of the importance of learning while working will be presented.

Coming into this project, I had never seen a DCP before. Upon first setting eyes on it, I was not impressed. The instrument had laid idle for two years. A good part of my first semester of research was trying to find a tank of argon gas, a proper regulator, fittings for the regulator, and tubing for the gas. After the argon was hooked up, I dismantled the entire sample injection and excitation region. Replacement of old pieces with new, and cleaning of all other parts took place. The plasma was then attempted to be lit. To get a stable plasma, the various pressure gauges had to be adjusted, until finally a stable, quiet, plasma was established.

The next hurdle was to gain experience on the instrument. Various problems arose, and with countless hours reading through the instruction manual and Stephen Lipsky's thesis, I was able to rectify these problems.

Once I was confident with my knowledge of the instrument and what the project entailed, I was ready to begin analyzing samples. Unfortunatley, the equipment I was working with was not ready. On several occassions, the plasma would decide to shut-off for no apperant reason. Other times, I would run out of gas, and be delayed

until a new shipment came.

This, though, is what undergraduate research is about. It's about set backs and triumphs, taking on responsibilities, and learning about chemistry.

The data collected for the four Thorne-Smith samples has shed some light on this unknown quantity of R_2O_3. The presence of chromic oxide in limestone should be taken seriously. In an acidic medium, this oxide can be brought into solution, mainly, the groundwater. Prediction of the concentrations of certain oxides in the ore was attempted by using the data available. For instance, if a correlation could be set between one oxide and another, or an oxide and the amount of silica present, this would be most beneficial. But there was no obvious relationship present.

Even though inter-ore composition relationships couldn't be found, there is an intra-ore semi-quantitative relationship present. Five separate limestone ores were analyzed, and they all had percentages of the oxides that are similar in orders of magnitude. This, I consider, is a success. For now, a model can be made of dolemitic limestone ore in general: 0.2 - 3. % iron (III) oxide, 0.2 - 0.3 % aluminum (III) oxide, 0.005 - 0.025 % chromium (III) oxide, 0.025 - 0.07 % manganese (IV) oxide, and 0.04 - 0.05 % tin (IV) oxide.

Appendix A: Diagrams

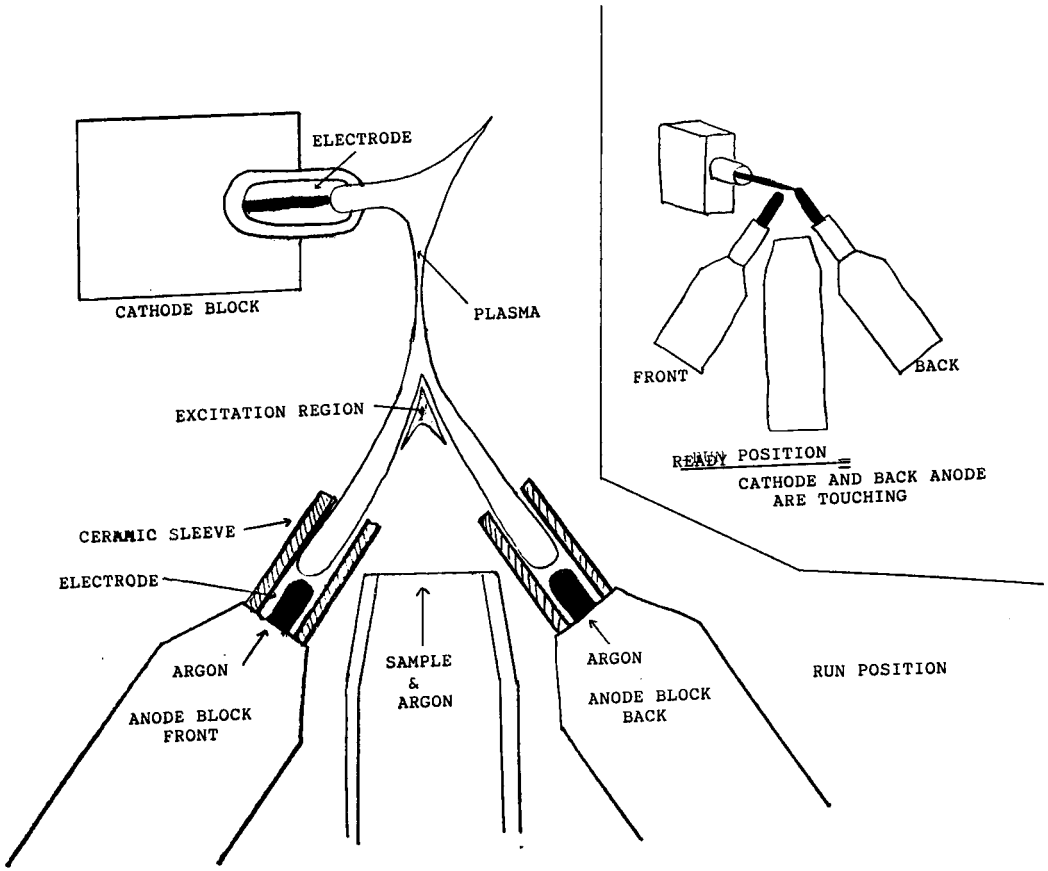
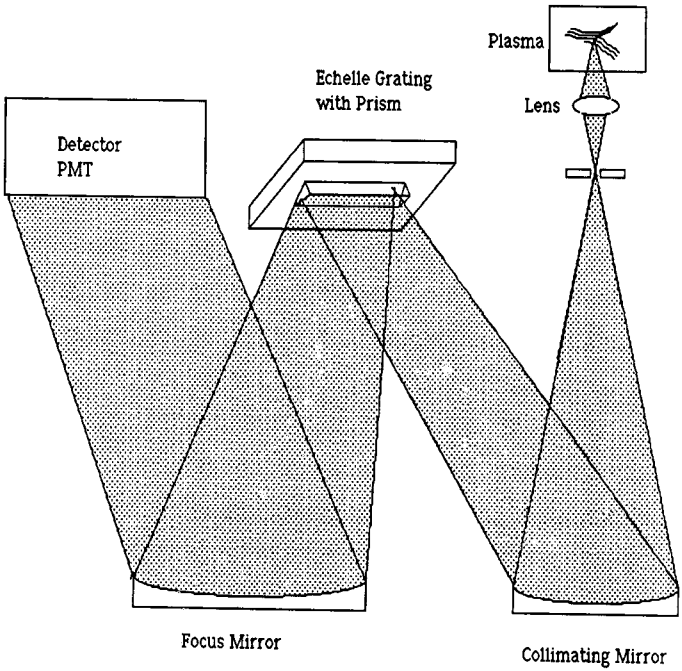

ELECTRODE
CATHODE BLOCK
PLASMA
EXCITATION REGION
CERAMIC SLEEVE
ELECTRODE
ARGON
ANODE BLOCK
FRONT
SAMPLE
&
ARGON
ARGON
ANODE BLOCK
BACK
RUN POSITION
FRONT
BACK
READY POSITION
CATHODE AND BACK ANODE
ARE TOUCHING

DIAGRAM 2.

Diagram 3



Reproduced from SpectraSpan,.Operating Manual

Cr

WAVELENGTH 357.869 nm
ORDER 63
STATE ATOM
PLASMA POSITION 0
ENTRANCE SLITS 50 × 300 μm
EXIT SLITS 100 × 300 μm
DETECTION LIMIT (DL) 0.002 mg/l = 2 ppb
LINEAR DYNAMIC RANGE (LDR) 0.02 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC) 0.07 mg/l
PRECISION (RSD) at 8 × BEC 1.4 %

COMMENTS

1. Mechanical restrictions - multielement cassettes:

   a. Ni at 341.476 (Order 66).
   b. Pd at 363.470 (Order 62).
   c. Rh at 369.236 (Order 61).
   d. Tl at 351.924 (Order 64).

2. Background high in organic matrices.

INTERFERENCE DATA

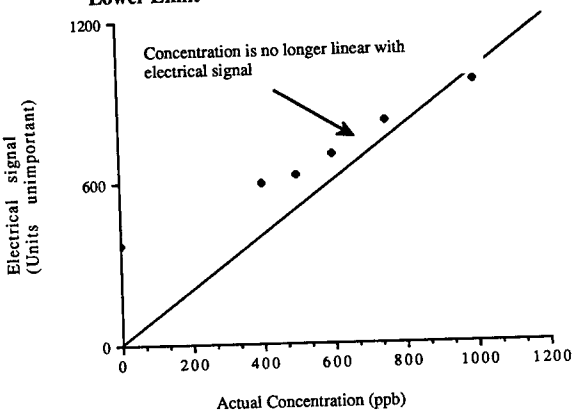
Equivalent Analyte Concentration, mg/l

Element	1000 mg/l
Aluminum	< DL
Calcium	0.009
Iron	0.04
Lithium	0.008
Magnesium	<DL

NOTES

Appendix B: Linear Dynamic Range

Linear Dynamic Range for Sn at 286.3 nm
Lower Limit



Appendix C: Helpful Hints

This is intended to aid those who plan to continue this research project, or use the DCP here at Union College. Several problems were encountered in this project, here is a list of suggestions to avoid them.

Be sure that the balances to be used are calibrated and operational.

Check purity of standards before using. Old standards may not be as pure as they state.

Remake dilute standards daily.

If plasma shuts off automatically, make sure the cooling water is flowing through the instrument. The current will shut off if the temperature gets too hot.

When pressing the PLS button, hold it in for a few seconds.

Lift the RUN/READY switch slowly.

The cathode ceramic sleeve has a tendency to get stuck in its holder. To avoid this, clean the cathode block of residue with 1M nitric acid.

The graphite electrodes are delicate, be careful.

The back anode and cathode blocks might cause some problems with their electrodes. Just watch out for them.

Appendix D: Calculations

Staistical Analysis:

Data: 49.7, 48.9, 50.4, 50.5, 49.4 — use T distribution.
Average: 49.8
Std. Dev: 0.7

95% Confidence error = 2.776 x Std Dev[18] — 2.776 x 0.7 = 1.9

1.9 / 49.8 = 0.038 ≈ 4% Error

Concentration of Standards:

ppt R = (g R / 100g Water) x 1000

g R = % R in Compound (by weight) x g Compound

% R = (MW R / MW Compound) x #R in Compound

For example ppt Cr in $K_2Cr_2O_7$:
% R = (51.996 / 294.19) x 2 = 0.3535
g R = 0.3535 x 0.2831 = .1001
ppt Cr = (.1001 / 100) x 1000 = 1.001

% R_2O_3 from ppm R:	%Fe_2O_3 in 24
g R = ppm / 10000	34.1/10000 = 0.00341
moles R = g R / MW R	0.00341/55.847 = 6.106×10^{-5}
moles R_2O_3 = 1/2 moles R	6.106×10^{-5} / 2 = 3.053×10^{-5}
g R_2O_3 = MW R_2O_3 x mol R_2O_3	159.6 x 3.053×10^{-5} = 0.004873
% R_2O_3 = (g R_2O_3 / g Sample) x 100	0.004873 / .2217 x 100 = 0.220%

Values for weights of samples:

24 - 0.2217g

25 - 0.2153g

26 - 0.2077g

27 - 0.2278g

local - 0.2085g

Endnotes:

[1] Edward D. Schroeder and George Tchobanoglous, Water Quality (Reading, Mass: Addison-Wesley Publishing Co., 1985) 405.

[2] Safe Drinking Water Committee, Advisory Center on Toxicology, Assembly of Life Sciences, National Research Council, Summary Report: Drinking Water and Health (Washington, DC: National Academy of Sciences, 1977) 20.

[3] Schroeder and Tchobanoglous, 45.

[4] Safe Drinking Water Committee, 20.

[5] Schroeder and Tchobanoglous, 721.

[6] Safe Drinking Water Committee, 24.

[7] Stephen N. Lipsky, The Use of Direct Current Argon Plasma Spectroscopy for Quantitative Analysis of Geological Samples (Schenectady, NY: Union College, 1987) 2.

[8] Douglas A. Skoog, Principles of Instrumental Analysis 3rd Ed. (Philadelphia, Pa: Saunders College Publishing, 1985) 294.

[9] Douglas A. Skoog, 296

[10] SpectraMetrics, SpectraSpan IV Emission Spectrometer Operating Manual, (Andover, Mass: SpectraMetrics Inc., SMI) 2.5.2.

[11] Andrew T. Zander, "DC Plasma Emission Spectrometry Speeds Elemental Analysis," Industrial Research and Development Feb. 1982 147-148.

[12] Skoog, 129-130.

[13] Skoog, 300.

[14] SpectraMetrics, 2.1.2.1.

[15] Skoog, 140.

[16] Lipsky, 22.

[17] Lipsky, 38.

[18] William Mendenhall, Dennis D. Wackerly, Richard L. Scheaffer, Mathematical Statisitcs with Application, 4th Ed., (Boston, Mass: PWS-Kent Publishing Co., 1990) 761.

Bibliography:

Lipsky, Stephen N. The Use of Direct Current Argon Plasma Spectroscopy for Quantitative Analysis of Geoligical Samples. Schenectady, NY: Union College, 1987.

Mendenhall, William, et al. Mathematical Statistics with Application 4th Ed. Boston, Mass: PWS-Kent Publishing Co., 1990.

"Physical Properties of Inorganic Compounds." Handbook of Chemistry and Physics 55th Ed. Ed. Robert C. Weast. Cleveland, Ohio: CRC Press, 1975.

Safe Drinking Water Committee, Advisory Center on Toxicology, Assembly of Life Sciences, National Research Council. Summary Report: Drinking Water and Health. Washington D.C: Nation Academy of Sciences, 1977.

Schroeder, Edward D. and George Tchobanoglous. Water Quality. Reading, Mass.: Addison-Wesley Publishing Co., 1985.

Skoog, Douglas A. Principles of Instrumental Analysis 3rd Ed. Philadelphia, Pa: Saunders College Publishing, 1985.

SpectraMetrics. SpectraSpan IV Emission Spectrometer Operating Manual. Andover, Mass: SpectraMetrics Inc., SMI.

Zander, Andrew T. "DC Plasma Emission Spectrometry Speeds Elemental Analysis." Industrial Research. Feb. 1982, 146-150.